

Remarks

In view of the above amendments and the following remarks, reconsideration of the outstanding office action is respectfully requested.

The possibility of constructing optoelectronic devices, full-color displays, and optical sensors based on silicon has generated tremendous interest in the preparation and characterization of light emitting silicon nanoparticles. Because the particles' luminescence properties are size-dependent, multiple colors can be produced using a single material. These particles also have exciting potential applications as fluorescent tags for biological imaging, as has been proposed for II-VI compound semiconductor nanoparticles. They can be brighter and much more stable to photobleaching than the organic dyes used in these applications, and they also have much broader excitation spectra, so that emission at multiple wavelengths (from particles of different sizes) can be excited by a single source. There are established methods for preparation of luminescent porous silicon, and aerosol synthesis of macroscopic quantities of non-luminescent silicon nanoparticles has been known for over 20 years. However, there are no reported methods for producing macroscopic quantities (i.e. more than a few milligrams) of luminescent silicon nanoparticles that are free from a substrate. Soon after the initial discovery of photoluminescence from porous silicon, Brus and co-workers published a series of papers in which they prepared silicon nanoparticles by high temperature decomposition of disilane. These studies were instrumental in building an understanding of photoluminescence mechanisms in silicon nanostructures. However, in their actual particle synthesis experiments, they collected less than 10 mg of particles per 24 hour day of reactor operation. Small quantities of luminescent silicon nanoparticles have been prepared by laser vaporization controlled condensation (LVCC).

Recently, Korgel and co-workers prepared brightly luminescent silicon nanoparticles in supercritical organic solvents at high temperature (500 °C) and pressure (345 bar). Again, they have produced beautiful and well-characterized particles, but in quite small quantities. In their first report, 0.2 ml per batch of 250-500 mM diphenylsilane was converted to silicon nanoparticles with a yield of 0.5% to 5%, which corresponds to 0.07 to 1.4 mg of Si nanoparticles per batch. Brightly luminescent silicon nanoparticles have been prepared by dislodging them from luminescent porous silicon wafers prepared electrochemically, and this has also generated tremendous technological and scientific

interest. However, this method also generates small quantities of silicon nanocrystals, and the emitting nanocrystals may be embedded in larger porous silicon particles.

The first solution phase synthesis of silicon nanoparticles was presented by Heath. More recently Kauzlarich and co-workers have demonstrated several procedures for producing silicon nanoparticles with a variety of surface terminations at mild conditions in solution using reactive Zintl salts. They are able to produce larger quantities of particles than the methods described in the previous paragraph. In some cases, they have shown blue-UV photoluminescence from these particles, but appear not to have observed the orange to red PL characteristic of porous silicon and most other nanoparticle preparation methods, including that presented here. Solid phase reactions have also been used to produce larger quantities of silicon nanoparticles, but apparently with much lower PL efficiency than the particles measured in the previous paragraph. Lam et al. produced silicon nanoparticles by the reaction of graphite with silicon dioxide (SiO_2) in a ball mill. A wide range of particle sizes were produced, but some PL was observed after ball milling for 7 to 10 days. Ostraat and co-workers have prepared oxide-capped silicon nanoparticles via vapor phase decomposition of highly diluted SiH_4 in nitrogen followed immediately by surface oxidation.

CO_2 laser pyrolysis of silane (SiH_4) is an effective method of producing gram-scale quantities of silicon nanoparticles, as first shown more than 20 years ago. It produces high-purity loosely agglomerated particles with controlled primary particle size and size distribution. Moreover, it is a continuous process that permits reasonable production rates. While several groups have synthesized silicon particles with this and similar methods, the resulting particles showed little or no visible photoluminescence. An exception to this is the work of Huisken and coworkers, who use pulsed CO_2 laser pyrolysis of silane, which yields luminescent particles, but in very small quantities. They have also studied the effect of particle aging in air and surface etching with HF on the photoluminescence spectrum.

In order to show efficient visible photoluminescence (PL), it is believed that silicon nanoparticles must be smaller than 5 nm, and their surface must be 'properly passivated' such that there are no non-radiative recombination sites on it. The mechanism(s) of photoluminescence in silicon nanocrystals and the effect of surface passivation on light emission from them remain topics of active research and debate. The size of silicon nanoparticles can be reduced by etching them in mixtures of hydrofluoric acid (HF) and nitric acid (HNO_3) as well as by aging them in air then removing the resulting oxide with HF.

The present invention is directed at overcoming these and other deficiencies in the art.

The objections to claims 35 and 36 are respectfully traversed in view of the above amendments.

The rejection of claims 1–25 and 27–34 under 35 U.S.C. § 102(a) for anticipation by Li, “Photothermal Aerosol Synthesis of and Photoluminescence from Silicon Nanoparticles,” *Annual Meeting Archive AICHE* 1284–1289 (November 3–8, 2002) (“the Li paper”) is respectfully traversed.

The Li paper was authored by inventors Mark D. Swihart, Xuegeng Li, and Yuanqing He, and non-inventor Suddha Talukdar. *See* Declaration of Mark T. Swihart, Ph.D. under 37 C.F.R. § 1.132 (“Swihart Declaration”) ¶ 4. Mr. Talukdar contributed to the development of a photothermal aerosol process for preparing luminescent silicon nanoparticles at the instruction of the inventors of the present application, but did not contribute to the conception of the invention as described and claimed. Swihart Declaration ¶ 7. Because Mr. Talukdar did not make the claimed invention, the Li paper (which is otherwise co-authored by the inventors of the present application) cannot be a printed publication before the applicants made the claimed invention. The Li paper is, therefore, not prior art under 35 U.S.C. § 102(a), and the anticipation rejection of claims 1–25 and 27–34 should be withdrawn.

The rejection of claims 1–3, 6, 7, 12–16, and 27–30 under 35 U.S.C. § 103(a) for obviousness over Botti, “Photoluminescence from Silicon Nanoparticles Synthesized by Laser-induced Decomposition of Silane,” *J. Appl. Phys.* 88(6):3396 (2000) (“Botti”) in view of Seraphin, “Influence of Nanostructure Size on the Luminescence Behavior of Silicon Nanoparticles Thin Film,” *J. Mater. Res.* 12(12):3386 (1997) (“Seraphin”) is respectfully traversed.

Botti discloses the synthesis of red- and yellow-emitting silicon nanoparticles in powder form by CO₂ laser heating of a silane-helium mixture.

Seraphin discloses the relation of size to peak photoluminescence emission wavelength in silicon nanoparticle thin films synthesized by pulsed laser ablation supersonic expansion. Chemical processing steps, including treatment with HF, HNO₃, and HF/HNO₃/H₂O solutions, are performed on the thin films to vary the size of the nanoparticles.

It is the U.S. Patent and Trademark Office's ("PTO") position that it would have been obvious to make silicon nanoparticles by CO₂ laser heating of a silane-helium mixture, as taught in Botti, and then to acid etch the silicon nanoparticles to shift the luminescent peak, as taught by Seraphin. Applicants respectfully disagree.

Botti and coworkers were aware of the teachings of Seraphin, as demonstrated by the fact that Botti cites Seraphin as reference number 17. Despite their apparent knowledge of Seraphin, the co-authors of Botti did not apply the etching method disclosed in Seraphin to their particles. The reason that Botti did not apply the etching techniques of Seraphin to the Botti process likely evolves from the fact that Seraphin etches wafers made from thin films of agglomerated silicon nanoparticles deposited on Teflon[®] substrates. On the other hand, Botti etches with particles. In view of the different forms of the material being etched in Botti and Seraphin, one of ordinary skill would not have applied the etching techniques of the latter to the particles of the former. This is evidenced not only by the fact that Botti does not utilize Seraphin's teachings (despite knowledge of them), but also by the fact that Seraphin, in carrying out its HF etching procedure on a wafer, does so for 60 seconds, while applicants teach etching particles with HF for longer periods of 15–38 minutes in Figure 5 of the present applicant and 2–30 minutes on page 10, line 3 of the specification. This difference between the etching rates for silicon nanoparticles and bulk silicon wafers indicates that the etching mechanisms for each are significantly different, and, therefore, teaches away from combining the teachings of Botti with Seraphin. For these reasons, the obviousness rejection of claims 1–3, 6, 7, 12–16, and 27–30 over Botti in view of Seraphin is improper and should be withdrawn.

The rejection of claims 4 and 5 under 35 U.S.C. § 103(a) for obviousness over Botti in view of Seraphin and Withrow, "Effects of Hydrogen in the Annealing Environment on Photoluminescence from Si Nanoparticles," *J. Appl. Phys.* 86(1):396 (1999) (abstract) ("Withrow") is respectfully traversed, because Withrow fails to overcome the above-noted deficiencies of Botti and Seraphin.

The rejection of claims 8 and 9 under 35 U.S.C. § 103(a) for obviousness over Botti in view of Seraphin and Ehbreh, "Deposition and Analysis of Carbon and Silicon Clusters Generated by Laser-induced Gas Phase Reaction," *Proc. SPIE* pp. 171–172 (1996) (abstract) ("Ehbreh") is respectfully traversed, because Ehbreh fails to overcome the above-noted deficiencies of Botti and Seraphin..

The rejection of claims 8 and 9 under 35 U.S.C. § 103(a) for obviousness over Botti in view of Seraphin, Huiskens, “Light-emitting Silicon Nanocrystals From Laser Pyrolysis,” *Advanced Materials* 14(24):1861 (2002) (“Huiskens”), and U.S. Patent No. 4,613,440 to Zupancic (“Zupancic”) is respectfully traversed, because Huiskens and Zupancic, either alone or in combination, fail to overcome the above-noted deficiencies of Botti and Seraphin.

The rejection of claims 17–21 and 26 under 35 U.S.C. § 103(a) for obviousness over Botti in view of Seraphin and U.S. Patent No. 6,585,947 to Nayfeh (“Nayfeh”) is respectfully traversed.

Nayfeh relates to a method for converting bulk silicon crystals into individual silicon nanoparticles. This method involves gradually advancing bulk silicon (e.g., a silicon wafer) into a chemical etch bath at a low speed while etching is taking place, in the presence of an external current, thus forming a meniscus at the interface of etchant solution and air. In one embodiment, silicon nanoparticles are then obtained by removing the silicon wafer from the etchant bath and rinsing it with methanol. The bulk wafer may also be subjected to ultrasound treatment that results in a precipitate of larger yellowish/orangish luminescent particles and a bluish colloid. The bluish colloid may be filtered with a 200nm filter to separate any remaining larger particles.

Claims 17–21 and 26 are patentable over Botti and Seraphin for the reasons discussed above with respect to claim 1, and Nayfeh fails to overcome the above-noted deficiencies of these references. Further, Nayfeh does not teach the procedure of claim 17 where silicon nanoparticles are dispersed in a solvent prior to acid etching. Instead, this references disperses particles from bulk porous silicon into solution *after electrochemical etching*.

With respect to claim 26, the PTO has cited Seraphin (page 3387, Experimental Conditions) as teaching “treating the isolated photoluminescent silicon nanoparticles under conditions effective to induce rapid thermal surface oxidation.” However, all Seraphin teaches is oxide formation by aging in air at ambient temperature or by chemical oxidation with nitric acid. Since Seraphin alone or in combination with Botti and Seraphin fails to teach rapid thermal surface oxidation, the combination of these references cannot be applied against claim 26.

For these reasons, the obviousness rejection of claims 17–21 and 26 over Botti, Seraphin, and Nayfeh is improper and should be withdrawn.

The rejection of claim 35 under 35 U.S.C. § 103(a) for obviousness over Botti in view of Seraphin and U.S. Patent No. 6,846,565 to Korgel (“Korgel”) is respectfully traversed.

Korgel relates to a method of preparing nanoparticles that involves reacting an organometallic precursor in the presence of a capping agent of the general formula $(R)_n-X$. Korgel teaches that the capping agent may prevent reactive degradation of the nanoparticles when exposed to chemical contamination.

Claim 35 is patentable over Botti and Seraphin for the reasons discussed above, and Korgel fails to overcome the above-noted deficiencies of these references. Moreover, Korgel teaches the inclusion of the capping agent in the particle synthesis process such that the particle formation and capping occur simultaneously. Thus, Korgel alone, or in combination with Botti and Seraphin, fails to teach treating photoluminescent silicon nanoparticles under conditions effective to produce photoluminescent silicon nanoparticles having a Si-H terminated surface, as claimed. For these reasons, the obviousness rejection of claim 35 over these references is improper and should be withdrawn.

The rejection of claim 36 under 35 U.S.C. § 103(a) for obviousness over Botti in view of Seraphin, Zou et al., “Surface Functionalization of Si Nanoclusters with Alkoxide and NMR Studies,” Abstract of paper presented in ACS National meetings (2003) (“Zou”), and Bocarsly, “Surface-chemical Control of Optical Quenching Process at Porous Silicon Interfaces: Generation of a Stable-selective Sulfur-dioxide Sensor,” Abstract of paper presented in ACS National meetings (2000) (“Bocarsly”) is respectfully traversed.

Zou discloses terminating chloride-capped silicon nanoclusters to give alkoxy-capped silicon nanoclusters.

Bocarsly teaches that the Si/SiO_x interface on oxidized silicon nanoparticles can be stabilized by modification with silylfluorocarbon.

Claim 36 is patentable over Botti and Seraphin for the reasons discussed above, and Zou and Bocarsly fail to overcome the above-noted deficiencies of these references. Additionally, Zou’s process starts from chloride-capped particles and, therefore, would not be applicable to Botti’s and Seraphin’s materials, which are not silicon capped. Accordingly, one of ordinary skill in the art would not have combined the teachings of these

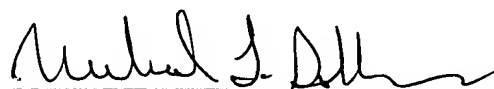
references. For these reasons, the obviousness rejection of claim 36 over Botti in view of Seraphin, Zou, and Bocarsly is improper and should be withdrawn.

In addition, applicants note that item 10 of the Office Action Summary was checked, but the PTO did not indicate (by checking sub-item 10.a or 10.b) whether the drawings filed on March 9, 2004, were accepted or objected to. Applicants respectfully request clarification on this issue.

In view of all of the foregoing, applicants submit that this case is in condition for allowance and such allowance is earnestly solicited.

Respectfully submitted,

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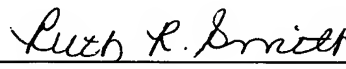
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